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13. ABSTRACT (Maximum 200 Words) The objective of this research program is to develop the chemistry and applications of a new biomimetic in situ synthetic system for the fabrication of inorganic/organic composite materials. The research focuses on understanding the mechanisms of the solid-state syntheses which give rise to composites in which the crystals of the inorganic phase are identical in size, morphology, and crystallographic orientation, the determining characteristics of naturally-formed biological composites. Synthesis of a new class of ordered composites, the high pressure lead sulfide phases, was carried out, and evaluation of these new materials' optoelectronic properties will be attempted. Synthesis of high-pressure phases of refractory ceramics such as boron nitride, will be attempted. An extension of the biomimetic synthetic process, an analogue of the solution sol-gel synthetic scheme for oxide ceramics, will also be studied in order to optimize a previously unknown process, the production of nonoxide ceramics by a solution sol-gel route. DTIC QUALITY INSPECTED 3				
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FINAL TECHNICAL REPORT

AFOSR Grant No.: F49620-95-I-0225

Title: Supramolecular Organization Using a Synthetic Analogue of Biomineralization

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Statement of Work

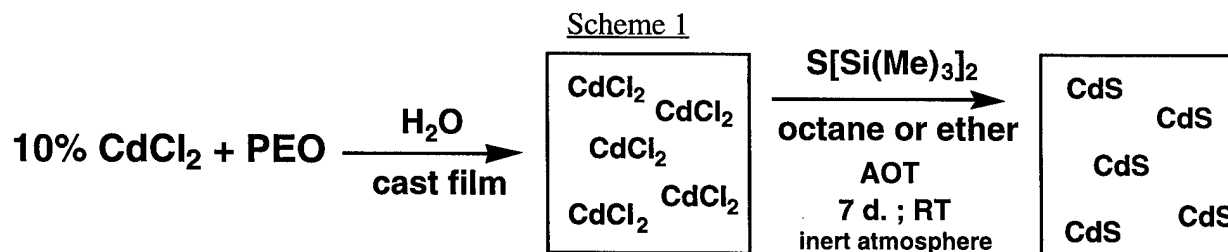
We will study a general method for the fabrication of biomimetic molecular-level composites. These inorganic/organic composites, while blended on the molecular level, will display the characteristic order and hierarchy of natural biominerals. These characteristics include regularity of size in the crystals of the inorganic phase, regularity of morphology in these crystals, and regularity in the crystals' crystallographic orientation. The synthesis method will be deliberately biomimetic, in that it will seek to copy in every way possible the biomineralization mechanisms of natural biological systems. These include an in situ synthesis of the inorganic phase, or a synthesis in which the inorganic crystals grow within the organic matrix, rather than a dispersion of the preformed particles in the organic resin. Also necessary to this biomimetic synthesis of composites is matrix mediation of nucleation, the control of crystal nucleation and growth by the polymer matrix. In order to achieve this mediation, we will use polymers which share the biologically important qualities of molecular preorganization and molecular complementarity, or structural organization and the ability to bind inorganic reagents. Using this fabrication method, we will study the mechanisms of growth of our synthetic crystals using a model system based on the crystallization of CdS and lead sulfides in poly(ethyleneoxide). We will determine the importance of various crystallization mechanisms and factors, such as reaction temperature, the chemical identity of polymer binding groups, the variation of the II-VI semiconductor to be crystallized, and the use of small molecules placed in the organic matrix and used to bind to and modify the growth and habit of the crystals.

Characterization of the biomimetic composites so synthesized will be aimed at determining not only the chemical identity of the products, but also their size, morphology, orientation, and solid-state structure. Methods of characterization will include FT-IR to identify products, scanning and transmission electron microscopy to determine size and morphology, quantitative EDAX spectroscopy to determine product stoichiometry, and xray and electron diffraction techniques to determine the phase and orientation of the crystalline products.

Status of Effort

Biological composite materials such as bones, teeth, and shells, consist of a polymeric matrix reinforced by an inorganic phase which forms within the matrix. These materials are distinguished from synthetic composites by the high degree of organization and regularity displayed by the inorganic phase. Inorganic minerals of uniform size, morphology, and crystallographic orientation can be formed in ordered arrays within living cells. Such a process has not been realized in synthetic systems, although recent strong interest in nanoscience has stimulated much research in the area. We have reported an example of a synthetic process which produces composite materials analogous to those produced by natural biomineralization. The inorganic/organic in-situ synthesized composites display controlled inorganic crystal size, morphology, and orientation, which characteristics are determining features of Type II, or matrix-mediated, biocomposites. The synthetic factors which we attempted to optimize in order to give biomimetic properties to synthetic composites were 1) strong binding by the organic matrix of the inorganic reagents (molecular complementarity), 2) good "solvation" of the inorganic reagents by the polymer, and 3) an ordered, regular polymer environment in which to induce nucleation (matrix preorganization). In this work we have studied the ordered crystallization process in greater detail and attempted to analyze the ways by which some of the variable synthetic factors present in this system affect the organization of the polymer-grown crystals obtained. Application of these factors may allow the fabrication of synthetic materials with the control, order, and regularity of biominerals, and open many opportunities for accessing unique materials and properties.

The crystallization system most studied was that of CdS formed in situ in a poly(ethyleneoxide) (PEO) polymer film, as shown in Scheme I:



Our principal findings are in three areas: 1) general factors controlling the crystallization of CdS in polymers, 2) surfactant effects on crystal growth and organization, and 3) matrix effects on crystal growth and organization.

Accomplishments/New Findings

Surfactant Effects on Crystal Growth and Organization

Our experiments demonstrate that the ligands added to the in situ crystallization reaction (the surfactant AOT, sodium bis(diethylsulfosuccinate), in Scheme I) are almost solely responsible for the nucleation and orientation of the CdS crystals. First, we have shown by x-ray photoelectron spectroscopy that the surfactant does indeed form a mono- or multilayer assembly on the polymer film's surface, as was previously hypothesized. That this is a surface monolayer, and that AOT is not incorporated into the bulk film, was shown by the failure of films which are cast from an AOT solution, rather than previously cast and subsequently exposed to AOT, to crystallize CdS. We have shown that this surface AOT interacts with the polymer-bound CdCl_2 on a molecular level: the normal crystalline diffraction pattern of the CdCl_2/PEO complexes formed in a solution-cast PEO film vanish when that film is subsequently exposed to AOT. The AOT therefore is binding or interacting with the polymer-bound Cd, altering its former crystalline structure. A new diffraction pattern is observed in the CdCl_2/PEO films when they are exposed to AOT; this could arise from formation of AOT/ CdCl_2 crystalline structures, or from the arrangement of surface AOT in a new crystalline lattice structure when it forms layers on the PEO surface. Experiments which will distinguish between these two possibilities are now in progress. We have also shown that little or no nucleation of CdS crystals in PEO films is seen without added AOT, even in films of optimum thickness (see below). Virtually without exception, all single crystals of CdS obtained with AOT in these syntheses, of whatever crystalline phase, are oriented on 001: these data demonstrate that the surfactant is primarily responsible for both crystal nucleation and crystallographic orientation. 001 is the crystallographic orientation most commonly seen in

biological systems, another feature which our synthetic system has successfully imitated. Since both the zinc blende and the rock salt structures of CdS (the phases we have seen as 001-oriented single crystals) present Cd-rich faces in this orientation, our data suggests that the binding of the sulfonate headgroup to polymer-bound Cd selects the orientation of the resulting crystal. Other surfactants we have examined have proved to be too insoluble in octane to use in the current synthetic reaction. Use of a surfactant with a carboxylic acid headgroup (arachidic acid), has not produced the same nucleation/orientation as did AOT. This is attributed to the weaker binding of the headgroup to the soft Cd^{+2} ions. Arachidic acid induces mineralization in characteristic morphologies very different than those seen with AOT, thereby demonstrating the importance of the surfactant in mediating mineralization. We have also shown that, contrary to what has been seen in crystallizations from solution under Langmuir-Blodgett monolayers, the surfactant in these syntheses does not determine the phase of the crystals produced. Under varying synthetic conditions (see below), we have produced both the zinc blende and rock salt phases of CdS with AOT. Crystal phase selection by lattice matching of the crystal to the interheadgroup spacing of the monolayer film is therefore not indicated.

Finally, we have demonstrated that the surfactant exerts great influence on the assembly of nucleated particles into macromolecular structures. Along with single crystals of CdS (invariably cubic or rectangular), large, very regular bipyramidal-shaped assemblies of CdS are seen in every film which has been exposed to AOT. The number of these structures increases almost linearly with increasing AOT concentration. Although perfectly regular in shape, these assemblies are not crystalline, producing only faint rings in electron diffraction studies. They appear to be formed of very small crystallites or amorphous particles assembled into regular bipyramidal shapes selected by the AOT. Upon long exposure to AOT, PEO films containing only CdCl_2 also form identically-shaped assemblies, demonstrating that it is the surfactant which is responsible for these assemblies and not some feature of the CdS synthetic reaction. This appears to be an example of the vectorial aggregation of amorphous or microcrystalline particles which, in biological systems, is responsible for the formation of macroscale organized composite structures, as, for example, the spines of sea

urchins. Our current data therefore suggest that AOT nucleates crystallites by binding to polymer-bound Cd atoms near the polymer surface. At low concentrations of AOT, possibly because the polymer film has areas where there is incontinuous coverage by the surfactant monolayer, growth of single crystals may arise from these individual nucleation sites. At higher concentrations of AOT, or in regions of the film which are more completely covered by a continuous monolayer, the individual nucleation sites may assemble into regular shapes (although not yet coalescing into single crystals), the structure of which are determined by the structure of the surface monolayer. Arachidic acid also produces regular shapes, completely different than those seen with AOT. We are currently investigating by SIMS whether AOT coverage on the film's surface correlates to production of bipyramidals in these areas. Other synthetic factors (see below) also determine which sort of macromolecular crystal or assembly will arise from individual nucleation sites. We are in addition investigating methods of inducing the bipyramidal aggregates to form single crystals, as is seen in biological systems.

Research has been extended to the synthesis of PbS in PEO matrices. This mineral has only one reported phase, the rock salt structure. When synthesized in solution, in "thick" polymer films, or in "thin" polymer films without surfactant, mineralization is disorganized; no regularity of shape or size in the PbS is seen. However, when synthesized in situ in thin films of PEO in the presence of AOT, along with some disorganized mineralization (identified by its diffraction pattern as poorly crystalline PbS), large crystals are also seen. These crystals adopt either hexagonal or tetragonal morphologies. Their diffraction patterns clearly indicate that they are not rock-salt phase PbS. However, their diffraction patterns are consistent with those reported for PbS₂, which adopts two known phases, one hexagonal and one tetragonal. This phase is stable at atmospheric pressure, but has previously been synthesized only at 70 kbar pressure. The preferential adoption of this high-pressure phase in the biomimetic synthetic conditions is similar to that seen in actual biological systems (such as seashells, in which metastable phases of CaCO₃ are often found), and is consistent with the CdS results, which suggested that the density of the matrix, or the "solid-state" effect, was responsible for the preferential growth of the rock salt high-pressure phase of

CdS. Further studies into the generality of the densification effect of the biomimetic synthetic system, to produce phases not usually seen at atmospheric conditions, are underway.

Personnel Supported and/or Associated With Research Effort

Patricia Bianconi	Associate Professor, principal investigator
Elizabeth Cates	Graduate student, Ph.D. candidate
Claire Likar	Graduate student, Ph.D. candidate
David Long	Graduate student, Ph.D. candidate
Brain Aldrich	Graduate student, Ph.D. candidate

Publications

1. Bianconi, P. A. "Biomimetic Mineralization", in Materials Chemistry: An Emerging Discipline, L. V. Interrante, L. A. Caspar, and A. B. Ellis, eds., American Chemical Society Symposium Series No. 245, Washington D. C. **1995**, 509 - 522.
2. Mark, J. E.; Lee, C. Y.; Bianconi, P. A., Eds., Hybrid Organic-Inorganic Composites, American Chemical Society Symposium Series, **1995**, 585.
3. Best, S. A.; Bianconi, P. A., Merz, K. M., "Structural Analysis of Carbyne Network Polymers", in Computer Aided Molecular Design, C.H. Reynolds, M. K. Halloway, and H. K. Cox, eds., American Chemical Society Symposium Series No. 589, **1995**, Chapter 22, 305 - 315.
4. Best, S. A.; Bianconi, P. A., Merz, K. M., "A Structural Analysis of Carbyne Network Polymers", *Journal of the American Chemical Society*, **1995**, *117*, 9521 - 9258.
5. Long, D. P. and Bianconi, P. A., "A Catalytic System for Ethylene Polymerization Based on Group III and Lanthanide Complexes of Tris(pyrazolyl)borate Ligands", *Journal of the American Chemical Society*, **1996**, *118*, 12453 - 12454.
6. Cates, E. and Bianconi, P. A. "Surfactant Nucleation and Orientation of Crystals in the Biomimetic Syntheses of Metal Sulfides in a Polymer Matrix", submitted to *Journal of the American Chemical Society*.
7. Cates, E. and Bianconi, P. A. "Formation of a Novel Lead Sulfide Phase at Low Pressure by a Biomimetic Synthetic Route", submitted to *Journal of the American Chemical Society*.

Interactions/Transitions

A. Participation/presentations at meetings, conferences, seminars, etc.

Invited lectures

- 1 "Crystallization of an Inorganic Phase Controlled by a Polymer Matrix", American Biophysical Society Meeting, San Francisco, CA, February 1995.
- 2 "Poly(phenylcarbyne): A Polymer Precursor To Diamond", Department of Chemistry, University of Toronto, Toronto, Ontario, March 1995.
- 3 "Poly(phenylcarbyne): A Polymer Precursor To Diamond", Argonne National Laboratory, Argonne, IL, April 1995.
- 4 "A Synthetic Analogue of the Biomineralization Process", Department of Chemistry, University of Massachusetts at Amherst, Amherst, MA, May 1995.
5. "Supramolecular Organization Using a Synthetic Analogue of Biomineralization", Air Force Office of Scientific Research, Wright-Patterson Air Force Base, Dayton, OH, August 1995.
- 6 "A Synthetic Analogue of the Biomineralization Process", IV International Conference on Materials, Cancun, Mexico, August 1995.
- 7 "Poly(phenylcarbyne): A Polymer Precursor To Diamond", Department of Chemistry, Florida State University, Tallahassee, FL, September 1995.
- 8 "A Synthetic Analogue of the Biomineralization Process", 211th National Meeting of the American Chemical Society, New Orleans, LA, March 1996.

Presentations at Meetings

1. "Lanthanide Alkyl and Hydride Complexes Containing The Trispyrazolylborate Ligand And Their Catalytic Activity With Olefins", D. P. Long, G. Randazzo, and P. A. Bianconi, 211th National Meeting of the American Chemical Society, New Orleans, LA, March 1996.
2. "Lanthanide Alkyl and Hydride Complexes Containing The Trispyrazolylborate Ligand And Their Catalytic Activity With Olefins", D. P. Long and P. A. Bianconi, 10th International Symposium on Homogeneous Catalysis, Princeton, NJ, August 1996.
3. "Poly(cyanocarbyne): Synthesis and Properties of a Water-Soluble Carbon Network-Backbone Polymer", S. A. Best and P. A. Bianconi, 1996 Fall Meeting of the Materials Research Society, Boston, MA, December 1996.
4. "Crystallization of Metal Oxides in a Polymer Film by a Biomimetic Synthetic Process", L. Kuhns and P. A. Bianconi, 1996 Fall Meeting of the Materials Research Society, Boston, MA, December 1996.

B. Consultive or Advisory Functions

None

C. Transitions

Move from Penn State University to the Univeristy of Massachusetts on Septmenber 1, 1996

New Discoveries, Inventions or Patent Disclosures

None

Honors/Awards

1994-1997	DuPont Young Professor Award
1994-1996	Alfred P. Sloan Research Fellowship
1992-1997	Camille and Henry Dreyfus Teacher/Scholar Award
1992-1994	Beckman Young Investigator Award